

## **Pd-Catalyzed Domino Carbonylative / Decarboxylative Allylation: An Easy and Selective Monoallylation of Ketones**

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### **Supplementary Information**

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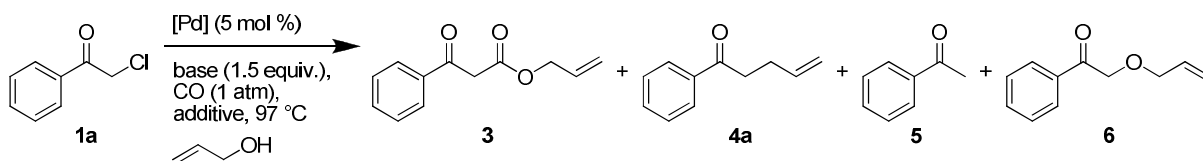
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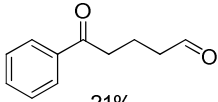
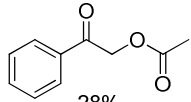
## I. Experimental Section

### General instrumentation:

All carbonylation and tandem reactions were carried out under a CO atmosphere. All other reactions were carried out under an argon atmosphere. Dry solvents were obtained from a Braun purification system MB SPS-800. Allyl alcohol was distilled and stored under an argon atmosphere. NMR spectra were recorded (Bruker 400 MHz or Bruker 300 MHz,  $^1\text{H}$ , and 101 MHz,  $^{13}\text{C}$ ) in  $\text{CDCl}_3$  (which also provided the lock signal at  $\delta = 7.26$  ppm for  $^1\text{H}$  and  $\delta = 77.16$  ppm for  $^{13}\text{C}$ ). IR spectra were recorded on a Bruker Tensor 27 apparatus. Silica gel (40-63  $\mu\text{m}$ ) was used for chromatographic purification. TLC plates were visualized under UV light and spraying with  $\text{KMnO}_4$  (5 % in water).

### Atmospheric pressure optimization:

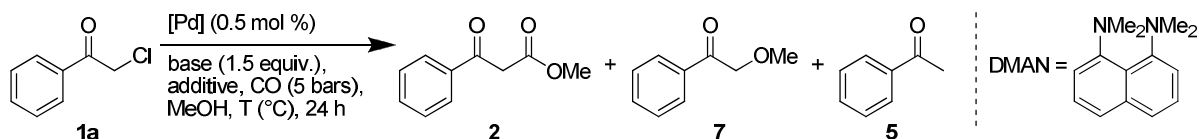


Catalyst	Base	Additive <sup>b</sup>	Products <sup>a</sup>
$\text{PdCl}_2(\text{PPh}_3)_2$	$\text{Et}_3\text{N}$	-	<b>5</b> (100%)
$\text{Pd}(\text{dba})_2 + \text{dppe}$	$\text{Et}_3\text{N}$	-	<b>5</b> (19%) + <b>6</b> (81%)
$\text{PdCl}_2\text{dppp}$	$\text{Et}_3\text{N}$	-	<b>5</b> (35%) + <b>6</b> (65%)
$\text{Pd}(\text{dba})_2 + \text{dppb}$	$\text{Et}_3\text{N}$	-	<b>5</b> (72%) + <b>6</b> (28%)
$\text{Pd}(\text{dba})_2 + 4 \text{PCy}_3$	$\text{Et}_3\text{N}$	-	<b>5</b> (27%) + <b>6</b> (73%)
$\text{Pd}(\text{dba})_2 + 4 \text{tfp}$	$\text{Et}_3\text{N}$	-	<b>5</b> (100%)
$\text{PdCl}_2(\text{PPh}_3)_2$	$\text{NaOAc}$	$\text{BnNEt}_3\text{Br}$	<b>5</b> (11%) +  21% +  28%

<sup>a</sup> Calculated on the basis of  $^1\text{H}$  NMR spectrum of the crude product. <sup>b</sup> 0.2 equiv. of additive is used.

Whatever the conditions used under an atmospheric pressure of CO, the desired product could not be isolated. Optimization of both steps was subsequently undertaken separately, the carbonylation reaction being carried out under 5 bars of CO.

### Optimization of the carbonylation step:

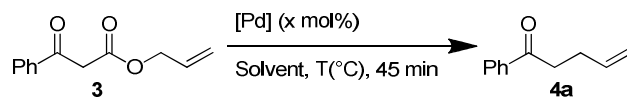


Catalyst	Base	Additive <sup>d</sup>	T (°C)	Products <sup>a</sup>
PdCl <sub>2</sub> (PPh <sub>3</sub> ) <sub>2</sub>	Et <sub>3</sub> N	-	100	<b>2</b> (16%) + <b>7</b> (18%) + <b>5</b> (66%)
PdCl <sub>2</sub> (PPh <sub>3</sub> ) <sub>2</sub>	Et <sub>3</sub> N	-	130	<b>7</b> (45%) + <b>5</b> (55%)
PdCl <sub>2</sub> (PPh <sub>3</sub> ) <sub>2</sub>	Bu <sub>3</sub> N	-	100	<b>2</b> (11%) + <b>7</b> (7%) + <b>5</b> (82%)
PdCl <sub>2</sub> (PPh <sub>3</sub> ) <sub>2</sub>	DMAN <sup>b</sup>	-	100	<b>2</b> (49%) <sup>c</sup> + <b>7</b> (6%) + <b>5</b> (45%)
PdCl <sub>2</sub> (PPh <sub>3</sub> ) <sub>2</sub>	DMAN <sup>b</sup>	BnNEt <sub>3</sub> Br	100	<b>2</b> (21%) + <b>7</b> (9%) + <b>5</b> (70%)
PdCl <sub>2</sub> dppf	DMAN <sup>b</sup>	-	100	<b>2</b> (16%) + <b>7</b> (8%) + <b>5</b> (76%)

<sup>a</sup> calculated on the basis of <sup>1</sup>H NMR spectrum of the crude product; <sup>b</sup> 1,8 bis(dimethylamino)naphthalene ; <sup>c</sup> isolated yield: 38%. <sup>d</sup> 0.2 equiv. of additive is used.

Under 5 bars of CO and using MeOH as the alcohol, up to 38% isolated yield of the desired methyl β-ketoester **2**, was obtained. However, extensive amounts of acetophenone **5** were also isolated, providing a proof for an inefficient carbonylation step.

### Optimization of the Pd-catalyzed decarboxylative allylation step:

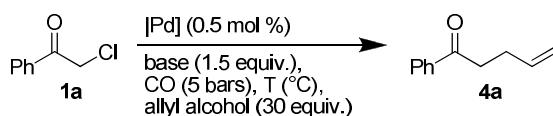


Catalyst	x (mol%)	Solvent	T (°C)	yield (%) <sup>a</sup>
Pd(dba) <sub>2</sub> + 4 PPh <sub>3</sub>	5	THF	60	64%
Pd(dba) <sub>2</sub> + 4 PPh <sub>3</sub>	5		90	72%
Pd(dba) <sub>2</sub> + 4 PPh <sub>3</sub>	5	Toluene	90	78%
-	-	Toluene	90	0%

<sup>a</sup> Isolated yields.

The Pd-catalyzed decarboxylative allylation proceeded smoothly, leading to the desired monoallylated ketone in good yield. In the absence of the palladium catalyst, the decarboxylative allylation did not take place, showing that the reaction did not occur *via* a thermal activation.

### Optimization of the *pseudo*-domino sequence:

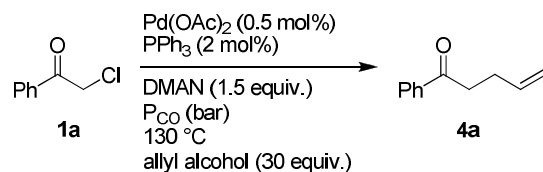


Catalyst	Base	T (°C)	yield (%) <sup>a</sup>
PdCl <sub>2</sub> (PPh <sub>3</sub> ) <sub>2</sub>	DMAN <sup>b</sup>	130	11
PdCl <sub>2</sub> dppf	DMAN <sup>b</sup>	130	19
Pd(OAc) <sub>2</sub> + 4 PPh <sub>3</sub>	DMAN <sup>b</sup>	130	20
Pd(OAc) <sub>2</sub> + dppb	DMAN <sup>b</sup>	130	12
Pd(OAc) <sub>2</sub> + dppf	DMAN <sup>b</sup>	130	1
Pd(OAc) <sub>2</sub> + 4 PPh <sub>3</sub>	Hünig's base	130	8
Pd(OAc) <sub>2</sub> + 4 PPh <sub>3</sub>	NaOAc	130	7

<sup>a</sup> isolated yields of **4a**. The mass balance to 100% is mainly acetophenone. <sup>b</sup> 1,8 bis(dimethylamino)naphthalene.

Whatever the conditions used under 5 bars of CO, it was not possible to achieve a yield higher than 20%. The influence of the CO pressure was therefore investigated.

### Optimization of the pressure:



P <sub>CO</sub> (bar)	5	10	15	20	25	30	50	80
yield (%) <sup>a</sup>	20	7	12	27	18	14	18	0

<sup>a</sup> Isolated yields of **4a**.

As previously observed,<sup>2</sup> an optimal pressure is observed in the range of 10 to 20 bars. In this case, the optimum is reached at 20 bars, yielding 27% of the monoallylated ketone.

### Ligands screening:

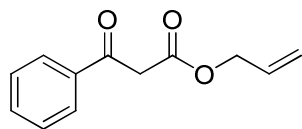
L	Yield (%) <sup>a</sup>
P( <i>t</i> -Bu) <sub>3</sub>	0
PCy <sub>3</sub>	13
PPh <sub>3</sub>	54
PPh <sub>2</sub> fur <sup>b</sup>	50
PPh(fur) <sub>2</sub> <sup>b</sup>	65
trifurylphosphine	76
P(OEt) <sub>3</sub>	13
dppf	0
XantPhos	56

<sup>a</sup> Isolated yields of **4a**. <sup>b</sup> fur = 2-furyl.

The screening of ligands showed that the more electron-poor the phosphine, the more efficient the reaction. Trifurylphosphine led to 76% yield of the desired product. Phosphites were however inefficient. XantPhos was the only efficient bidentate ligand.

<sup>2</sup> A. L. Lapidus, O. L. Eliseev, T. N. Bondarenko, O. E. Sizan, E. G. Ostapenko, and I. P. Beletskaya, *Kinetics and Catalysis*, 2004, **45**, 234.

## II. Characterization:



### *Allyl 3-oxo-3-phenylpropanoate (3)*

A flask was charged with methyl 3-oxo-3-phenylpropanoate **3** (1.45 g, 8.15 mmol, 1 equiv.), DMAP (301.8 mg, 2.45 mmol, 0.3 equiv.) and allyl alcohol (6 mL, 87mmol, 10 equiv.). The reaction was stirred at 90 °C for 3 days. The solution was concentrated *in vacuo*. The reaction was hydrolyzed and extracted with ethylacetate. The combined organic layers were dried over MgSO<sub>4</sub> and concentrated *in vacuo*. The residue was purified by column chromatography on silica gel (eluent: cyclohexane/AcOEt = 95/5) and yielded 0.875 g (53%) of the expected product **3** as a colorless oil.

Data for **3**:

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.97-7.94 (m, 1H), 7.80-7.77 (m, 1H), 7.62-7.58 (m, 1H), 7.51-7.40 (m, 2H), 5.90 (ddt, *J* = 5.7, 10.2, 17.2 Hz, 1H), 5.36-5.20 (m, 2H), 4.65 (dt, *J* = 1.3, 5.7 Hz, 2H), 4.03 (s, 2H); **HRMS** (ESI) *m/z* calcd. for C<sub>12</sub>H<sub>12</sub>NaO<sub>3</sub> [*M* + Na<sup>+</sup>] 227.0673, found 227.0679.

These data are in good agreement with those reported in the literature.<sup>3</sup>

### Chlorination of ketones:

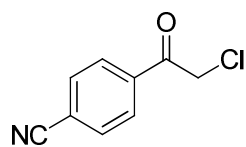
General procedure for the chlorination of ketones: according to the literature:<sup>4</sup>

A flask was charged with the substrate (4 mmol), NCS (4 mmol, 1 equiv.), and PTSA (0.4 mmol, 0.1 equiv.). The reaction mixture was heated to 80 °C overnight. The reaction was hydrolyzed and extracted with CH<sub>2</sub>Cl<sub>2</sub> (3x10 mL). The combined organic layers were dried over MgSO<sub>4</sub> and concentrated under reduced pressure. The crude reaction mixture was purified by silica gel column chromatography.

<sup>3</sup> J. S. Yadav, B. V. S. Reddy, A. D. Krishna, C. S. Reddy, and A. V. Narsaiah, *J. Mol. Catal. A: Chemical*, 2007, **261**, 93.

<sup>4</sup> I. Pravst, M. Zupan, and S. Stavber, *Tetrahedron*, 2008, **64**, 5191.





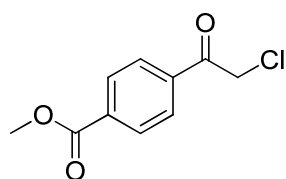
**4-(2-Chloroacetyl)benzonitrile (1d)**

Crude product was purified by column chromatography (eluent: CH<sub>2</sub>Cl<sub>2</sub>/cyclohexane = 3/7). The desired compound was isolated as a white solid (461 mg, 65%).

Data for **1d**:

**IR** (ATR Diamond): 3048, 2928, 2855, 2232, 1706, 1398, 1208, 830 cm<sup>-1</sup>; **<sup>1</sup>H NMR** (300 MHz, CDCl<sub>3</sub>) δ 8.08 – 8.06 (m, 2H), 7.84 – 7.81 (m, 2H), 4.68 (s, 2H). **<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>) δ 190.1, 137.2, 132.8, 129.2, 117.7, 117.4, 45.5. **HRMS** (ESI) m/z calcd. for C<sub>9</sub>H<sub>6</sub>ClNNaO [M + Na<sup>+</sup>] 202.0030, found 202.0037. **M.p.** = 90 °C (lit. = 91-95 °C).<sup>5</sup>

These data are in good agreement with those reported in the literature.<sup>6</sup>



**Methyl 4-(2-chloroacetyl)benzoate (1e)**

Crude product was purified by column chromatography (eluent: CH<sub>2</sub>Cl<sub>2</sub>/cyclohexane = 10/1). The desired compound was isolated as white crystals (535 mg, 63%).

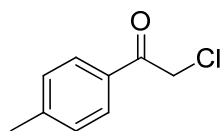
Data for **1e**:

**IR** (ATR Diamond): 3001, 2947, 1704, 1432, 1401, 1279, 1196, 1108, 762 cm<sup>-1</sup>; **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 8.18 – 8.15 (m, 2H), 8.04 – 8.01 (m, 2H), 4.73 (s, 2H), 3.97 (s, 3H). **<sup>13</sup>C**

<sup>5</sup> G. A. Russell and F. Ros, *J. Am. Chem. Soc.* 1985, **107**, 2506.

<sup>6</sup> See: P. R. Olivato, S. A. Guerrero, and R. Rittner, *Magnetic Resonance in Chemistry*, 1987, **25**, 179 for <sup>13</sup>C spectrum and: W. Szymanski, C. P. Postema, C. Tarabiono, F. Berthiol, L. Campbell-Verduyn, S. de Wildeman, J. G. de Vries, B. L. Feringa, and D. B. Janssen, *Adv. Synth. Catal.* 2010, **352**, 2111. R. D. Rieke, J. D. Brown and X. Wu, *Synth. Commun.* 1995, **25**, 3923 for <sup>1</sup>H spectrum

**NMR** (101 MHz, CDCl<sub>3</sub>)  $\delta$  190.6, 165.9, 137.3, 134.6, 130.0, 128.4, 52.5, 45.8. **HRMS** (ESI)  $m/z$  calcd. for C<sub>10</sub>H<sub>9</sub>ClNaO<sub>3</sub> [M + Na<sup>+</sup>] 235.01324, found 235.01325. **M.p.** = 136 °C.



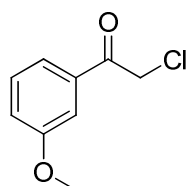
**2-Chloro-1-*p*-tolylethanone (1g)**

Crude product was purified by column chromatography (eluent: CH<sub>2</sub>Cl<sub>2</sub>/cyclohexane = 10/1). It afforded the desired compound as a brown solid (539 mg, 80%).

Data for **1g**:

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.87 (d,  $J$  = 8.3 Hz, 2H), 7.30 (d,  $J$  = 8.1 Hz, 2H), 4.69 (s, 2H), 2.44 (s, 3H). **<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>)  $\delta$  190.8, 145.1, 131.9, 129.7, 128.7, 46.0, 21.8. **M.p.** = 41 °C.

These data are in good agreement with those reported in the literature.<sup>7</sup>



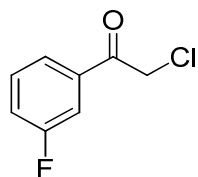
**2-Chloro-1-(3-methoxyphenyl)ethanone (1j)**

Crude product was purified by column chromatography (eluent: CH<sub>2</sub>Cl<sub>2</sub>/cyclohexane = 8/2). It afforded the title compound as a dark red solid (417 mg, 56%).

Data for **1j**:

**IR** (ATR Diamond): 2979, 2941, 2844, 1697, 1574, 1433, 1247, 1003, 777 cm<sup>-1</sup>; **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.54 – 7.47 (m, 2H), 7.40 (t,  $J$  = 7.9 Hz, 1H), 7.16 (ddd,  $J$  = 8.2, 2.6, 0.9 Hz, 1H), 4.70 (s, 2H), 3.86 (s, 3H). **<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>)  $\delta$  190.9, 160.1, 135.6, 129.9, 121.0, 120.5, 112.9, 55.6, 46.2. **HRMS** (ESI)  $m/z$  calcd. for C<sub>9</sub>H<sub>9</sub>ClNaO<sub>2</sub> [M + Na<sup>+</sup>] 207.01833, found 207.01836. **M.p.** = 60 °C.

<sup>7</sup> R. N. Ram and T. P. Manoj, *J. Org. Chem.* 2008, **73**, 5633.

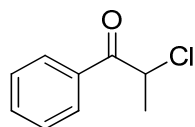


**2-Chloro-1-(3-fluorophenyl)ethanone (1i)**

Crude product was purified by column chromatography (eluent: CH<sub>2</sub>Cl<sub>2</sub>/cyclohexane = 8/2). It afforded the desired compound as a colorless oil (200 mg, 29%).

Data for **1i**:

**IR** (ATR Diamond): 3077, 2946, 1706, 1589, 1484, 1245 cm<sup>-1</sup>; **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.78 – 7.62 (m, 2H), 7.50 (td, *J* = 8.0, 5.5 Hz, 1H), 7.33 (tdd, *J* = 8.2, 2.6, 0.9 Hz, 1H), 4.68 (s, 2H). **<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>) δ 190.1, 163.0 (d, *J* = 249.0 Hz), 136.3 (d, *J* = 6.4 Hz), 130.7 (d, *J* = 7.7 Hz), 124.4 (d, *J* = 3.1 Hz), 121.2 (d, *J* = 21.4 Hz), 115.5 (d, *J* = 22.7 Hz), 45.8. **HRMS** (ESI) *m/z* calcd. for C<sub>8</sub>H<sub>6</sub>ClFNaO [*M* + Na<sup>+</sup>] 194.99834, found 194.99804.



**2-Chloro-1-phenylpropan-1-one (1m)**

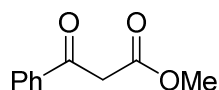
Crude product was purified by column chromatography (eluent: CH<sub>2</sub>Cl<sub>2</sub>/cyclohexane = 10/1). It delivered the title compound as a yellow oil (572 mg, 85%).

Data for **1m**:

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 8.02 (dd, *J* = 8.5, 1.3 Hz, 2H), 7.62 – 7.58 (m, 1H), 7.52 – 7.48 (m, 2H), 5.26 (q, *J* = 6.7 Hz, 1H), 1.75 (d, *J* = 6.7 Hz, 3H). **<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>) δ 193.7, 134.2, 133.8, 129.0, 128.8, 52.9, 20.0.

These data are in good agreement with those reported in the literature.<sup>8</sup>

<sup>8</sup> S. Hajra, M. Bhowmick, B. Maji, and D. Sinha, *J. Org. Chem.* 2007, **72**, 4872.



**Methyl 3-oxo-3-phenylpropanoate (2)**

Reaction performed with  $\alpha$ -chloroacetophenone **1a** (309.3 mg, 2.00 mmol, 1.0 equiv.),  $\text{PdCl}_2(\text{PPh}_3)_2$  (7.4 mg, 0.01 mmol, 0.5 mol%), methanol (5 mL) and 1,8-bis(dimethylamino)naphthalene (642.2 mg, 3.00 mmol, 1.5 equiv.) at 100 °C for 24 h. The residue was purified by column chromatography on silica gel (eluent: cyclohexane/AcOEt = 90/10) and yielded 134 mg (38%) of the expected keto-ester **2** as a colorless oil.

Data for **2**:

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.95 – 7.93 (m, 2H), 7.61 – 7.57 (m, 1H), 7.50 – 7.46 (m, 2H), 4.00 (s, 2H), 3.75 (s, 3H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  192.4, 168.0, 136.0, 133.9, 128.9, 128.6, 52.5, 45.8.

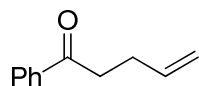
These data are in good agreement with those reported in the literature.<sup>9</sup>

**Domino Sequence: Pd-catalyzed Carbonylation / Decarboxylative Allylation**

General procedure for the domino sequence:

The autoclave was charged with  $\alpha$ -chloroketone **1a-n** (1 mmol, 1 equiv.),  $\text{Pd}(\text{OAc})_2$  (0.1 mmol, 0.1 equiv.), tri (2-furyl)phosphine (0.4 mmol, 0.4 equiv.), tributylamine (1.5 mmol, 1.5 equiv.), allyl alcohol (14.6 mmol, 15 equiv.) and toluene (1.5 mL). The autoclave was purged with CO and then pressurized (20 bars). The reaction mixture was warmed to 130 °C for 2 h. After cooling to room temperature, the pressure was carefully released and the autoclave vented. The reaction was concentrated *in vacuo*, hydrolyzed and extracted with diethyl ether. The combined organic layers were dried over  $\text{MgSO}_4$  and concentrated *in vacuo*.

<sup>9</sup> T. Taniguchi, Y. Sugiura, H. Zaimoku, and H. Ishibashi, *Angew. Chem. Int. Ed.* 2010, **49**, 10154.



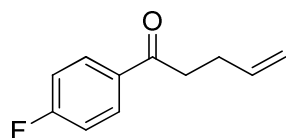
**1-Phenylpent-4-en-1-one (4a)**

Reaction performed with  $\alpha$ -chloroacetophenone **1a** (153.1 mg, 0.99 mmol, 1 equiv.) and allyl alcohol (1 mL, 14.6 mmol, 15 equiv.). The residue was purified by column chromatography on silica gel (eluent: cyclohexane/AcOEt = 95/5) and yielded 121 mg (76%) of the expected product **4a** as a yellow oil.

Data for **4a**:

**IR** (ATR Diamond): 3062, 2920, 1684, 1597, 1448, 1208, 913, 690  $\text{cm}^{-1}$ ;  **$^1\text{H}$  NMR** (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.85 – 7.83 (m, 2H), 7.44 – 7.40 (m, 1H), 7.35 – 7.31 (m, 2H), 5.79 (ddt,  $J$  = 16.8, 10.2, 6.5 Hz, 1H), 4.97 (dq,  $J$  = 17.1, 1.6 Hz, 1H), 4.90 (ddd,  $J$  = 10.2, 3.0, 1.3 Hz, 1H), 2.96 – 2.92 (m, 2H), 2.41 – 2.35 (m, 2H).  **$^{13}\text{C}$  NMR** (101 MHz,  $\text{CDCl}_3$ )  $\delta$  199.3, 137.3, 137.0, 133.0, 128.6, 128.0, 115.2, 37.7, 28.1. **HRMS** (ESI)  $m/z$  calcd. for  $\text{C}_{11}\text{H}_{12}\text{NaO}$  [ $\text{M} + \text{Na}^+$ ] 183.0778, found 183.0780.

These data are in good agreement with those reported in the literature.<sup>10</sup>



**1-(4-Fluorophenyl)pent-4-en-1-one (4b)**

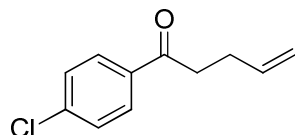
Reaction performed with 2-chloro-1-(4-fluorophenyl)ethanone **1b** (171.6 mg, 0.99 mmol, 1 equiv.) and allyl alcohol (1 mL, 14.6 mmol, 15 equiv.). The residue was purified by column chromatography on silica gel (eluent: cyclohexane/AcOEt = 90/10) and yielded 115 mg (65%) of the expected product **4b** as a yellow oil.

Data for **4b**:

**IR** (ATR Diamond): 3076, 2924, 2358, 1686, 1598, 1506, 1411, 1361, 1230, 1156, 984, 916, 841  $\text{cm}^{-1}$ ;  **$^1\text{H}$  NMR** (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.01 – 7.98 (m, 2H), 7.16 – 7.10 (m, 2H), 5.90 (ddt,  $J$  = 16.9, 10.2, 6.5 Hz, 1H), 5.09 (dq,  $J$  = 17.2, 1.6 Hz, 1H), 5.02 (dd,  $J$  = 10.2, 1.3 Hz, 1H),

<sup>10</sup> Y. Zhang and T. Rovis, *J. Am. Chem. Soc.* 2004, **126**, 15964.

3.05 (t,  $J = 7.3$  Hz, 2H), 2.53 – 2.47 (m, 2H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  197.8, 165.8 (d,  $J = 254.5$  Hz), 137.2, 133.4, 130.7 (d,  $J = 9.2$  Hz), 115.7 (d,  $J = 38.8$  Hz), 115.6, 37.7, 28.2. HRMS (ESI)  $m/z$  calcd. for  $\text{C}_{11}\text{H}_{11}\text{FNaO}$  [ $\text{M} + \text{Na}^+$ ] 201.06861, found 201.06839.



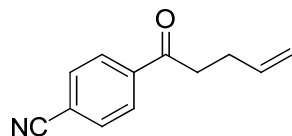
**1-(4-Chlorophenyl)pent-4-en-1-one (4c)**

Reaction performed with 2-chloro-1-(4-chlorophenyl)ethanone **1c** (190.3 mg, 1.01 mmol, 1 equiv.) and allyl alcohol (1 mL, 14.6 mmol, 15 equiv.). The residue was purified by column chromatography on silica gel (eluent: cyclohexane/AcOEt = 90/10) and yielded 112 mg (57%) of the expected product **4c** as a yellow oil.

Data for **4c**:

IR (ATR Diamond): 3076, 2919, 2358, 1687, 1643, 1403, 1206, 1093, 980, 915, 834  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.91 – 7.88 (m, 2H), 7.45 – 7.41 (m, 2H), 5.89 (ddt,  $J = 16.8, 10.2, 6.5$  Hz, 1H), 5.09 (dq,  $J = 17.1, 1.6$  Hz, 1H), 5.02 (dq,  $J = 10.2, 1.3$  Hz, 1H), 3.06 – 3.02 (m, 2H), 2.52 – 2.46 (m, 2H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  198.2, 139.5, 137.1, 135.3, 129.5, 129.0, 115.5, 37.8, 28.1. HRMS (ESI)  $m/z$  calcd. for  $\text{C}_{11}\text{H}_{11}\text{ClNaO}$  [ $\text{M} + \text{Na}^+$ ] 217.03906, found 217.03879.

These data are in good agreement with those reported in the literature.<sup>12</sup>



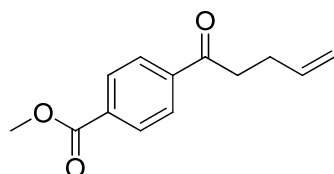
**4-Pent-4-enoylbenzonitrile (4d)**

Reaction performed with 4-(2-chloroacetyl)benzonitrile **1d** (166.7 mg, 0.92 mmol, 1 equiv.) and allyl alcohol (1 mL, 14.6 mmol, 15 equiv.). The residue was purified by column chromatography on silica gel (eluent: pentane/ $\text{CH}_2\text{Cl}_2$  = 20/80) but afforded a mixture of the product **4d** and 4-acetylbenzonitrile.  $^1\text{H}$  NMR with butadiene sulfone as internal standard allows to calculate 51 mg (30%) of the expected product **4d**.

Data for **4d**:

**IR** (ATR Diamond): 3077, 2923, 2358, 2231, 1691, 1405, 1282, 1206, 985, 917, 848  $\text{cm}^{-1}$ ;  **$^1\text{H}$  NMR** (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.06 – 8.04 (m, 2H), 7.85 – 7.76 (m, 2H), 5.89 (ddt,  $J$  = 16.8, 10.2, 6.5 Hz, 1H), 5.09 (dq,  $J$  = 17.1, 1.6 Hz, 1H), 5.03 (dq,  $J$  = 10.2, 1.2 Hz, 1H), 3.09 (t,  $J$  = 7.3 Hz, 2H), 2.54 – 2.48 (m, 2H).  **$^{13}\text{C}$  NMR** (101 MHz,  $\text{CDCl}_3$ )  $\delta$  198.1, 134.0, 136.8, 132.6, 128.6, 118.4, 116.5, 115.9, 38.2, 27.9. **HRMS** (ESI)  $m/z$  calcd. for  $\text{C}_{12}\text{H}_{11}\text{NNaO}$  [ $\text{M} + \text{Na}^+$ ] 208.07329, found 208.07308.

These data are in good agreement with those reported in the literature.<sup>11</sup>



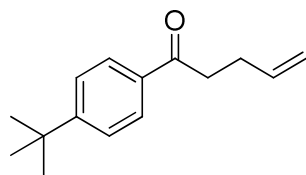
***Methyl 4-pent-4-enoylbenzoate (4e)***

Reaction performed with methyl 4-(2-chloroacetyl)benzoate **1e** (212.9 mg, 1.00 mmol, 1 equiv.) and allyl alcohol (1 mL, 14.6 mmol, 15 equiv.). The residue was purified by column chromatography on silica gel (eluent: pentane/ $\text{CH}_2\text{Cl}_2$  = 20/80) and yielded 87 mg (40%) of the expected product **4e** as a yellow powder.

Data for **4e**:

**IR** (ATR Diamond): 3077, 2956, 1718, 1675, 1568, 1568, 1432, 1274, 1195, 1104, 755  $\text{cm}^{-1}$ ;  **$^1\text{H}$  NMR** (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.13 (d,  $J$  = 8.6 Hz, 2H), 8.01 (d,  $J$  = 8.6 Hz, 2H), 5.91 (ddt,  $J$  = 16.8, 10.2, 6.5 Hz, 1H), 5.10 (dq,  $J$  = 17.1, 1.6 Hz, 1H), 5.03 (dq,  $J$  = 10.2, 1.3 Hz, 1H), 3.96 (s, 3H), 3.11 (t,  $J$  = 7.3 Hz, 2H), 2.54 – 2.49 (m, 2H).  **$^{13}\text{C}$  NMR** (101 MHz,  $\text{CDCl}_3$ )  $\delta$  199.0, 166.3, 140.2, 137.1, 133.9, 129.9, 128.0, 115.6, 52.6, 38.2, 28.1. **HRMS** (ESI)  $m/z$  calcd. for  $\text{C}_{13}\text{H}_{14}\text{NaO}_3$  [ $\text{M} + \text{Na}^+$ ] 241.08323, found 241.08352. **M.p.** = 73 °C.

<sup>11</sup> D. M. Hodgson, P. G. Humphreys, S. M. Miles, C. A. J. Brierley, and J. G. Ward, *J. Org. Chem.*, 2007, **72**, 10009.

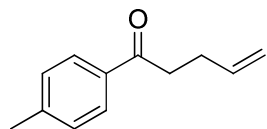


**1-(4-*tert*-Butylphenyl)pent-4-en-1-one (4f)**

Reaction performed with 2-chloro-1-(4-*tert*-butylphenyl)ethanone **1f** (212.9 mg, 1.01 mmol, 1 equiv.) and allyl alcohol (1 mL, 14.6 mmol, 15 equiv.). The residue was purified by column chromatography on silica gel (eluent: cyclohexane/AcOEt = 90/10) and yielded 118 mg (54%) of the expected product **4f** as a yellow oil.

Data for **4f**:

**IR** (ATR Diamond): 3075, 2961, 2358, 1683, 1606, 1407, 1269, 1107, 913  $\text{cm}^{-1}$ ;  **$^1\text{H}$  NMR** (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.93 – 7.90 (m, 2H), 7.50 – 7.47 (m, 2H), 5.92 (ddt,  $J$  = 16.8, 10.2, 6.5 Hz, 1H), 5.10 (dq,  $J$  = 17.1, 1.6 Hz, 1H), 5.02 (dq,  $J$  = 10.2, 1.3 Hz, 1H), 3.08 – 3.05 (m, 2H), 2.54 – 2.48 (m, 2H), 1.35 (s, 9H).  **$^{13}\text{C}$  NMR** (101 MHz,  $\text{CDCl}_3$ )  $\delta$  199.2, 156.8, 137.5, 134.5, 128.1, 125.6, 115.3, 37.7, 35.2, 31.2, 28.3. **HRMS** (ESI)  $m/z$  calcd. for  $\text{C}_{15}\text{H}_{20}\text{NaO}$  [ $\text{M} + \text{Na}^+$ ] 239.14064, found 239.14067.



**1-*p*-Tolyl-pent-4-en-1-one (4g)**

Reaction performed with 2-chloro-1-*p*-tolylethanone **1g** (170.2 mg, 1.00 mmol, 1 equiv.) and allyl alcohol (1 mL, 14.6 mmol, 15 equiv.). The residue was purified by column chromatography on silica gel (eluent: cyclohexane/ $\text{CH}_2\text{Cl}_2$  = 20/80) and yielded 77 mg (44%) of the expected product **4g** as a yellow oil.

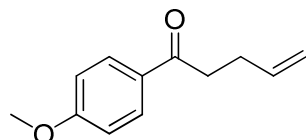
Data for **4g**:

**IR** (ATR Diamond): 2921, 1681, 1607, 1411, 1359, 1277, 1181, 1114, 979, 913, 810  $\text{cm}^{-1}$ ;  **$^1\text{H}$  NMR** (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.88 (d,  $J$  = 8.3 Hz, 2H), 7.27 (d,  $J$  = 8.1 Hz, 2H), 5.92 (ddt,  $J$  = 16.8, 10.2, 6.5 Hz, 1H), 5.09 (dq,  $J$  = 17.1, 1.6 Hz, 1H), 5.02 (dq,  $J$  = 10.2, 1.3 Hz, 1H), 3.08 – 3.04 (m, 2H), 2.53 – 2.47 (m, 2H), 2.42 (s, 3H).  **$^{13}\text{C}$  NMR** (101 MHz,  $\text{CDCl}_3$ )  $\delta$  199.2, 143.8,



137.5, 134.6, 129.4, 128.3, 115.3, 37.7, 28.4, 21.7. **HRMS** (ESI)  $m/z$  calcd. for  $C_{12}H_{14}NaO$   $[M + Na^+]$  197.09369, found 197.09368.

These data are in good agreement with those reported in the literature.<sup>12</sup>



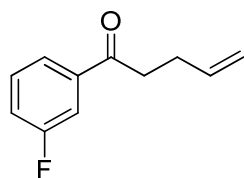
***1-(4-Methoxyphenyl)pent-4-en-1-one (4h)***

Reaction performed with 2-chloro-1-(4-methoxyphenyl)ethanone **1h** (184 mg, 1.00 mmol, 1 equiv.) and allyl alcohol (1 mL, 14.6 mmol, 15 equiv.). The residue was purified by column chromatography on silica gel (eluent: cyclohexane/AcOEt = 90/10) and yielded 146 mg (77%) of the expected product **4h** as a yellow oil.

Data for **4h**:

**IR** (ATR Diamond): 3074, 2928, 2843, 1676, 1601, 1511, 1256, 1172, 1028, 836  $cm^{-1}$ ; **<sup>1</sup>H NMR** (400 MHz,  $CDCl_3$ )  $\delta$  7.96 – 7.92 (m, 2H), 6.95 – 6.91 (m, 2H), 5.90 (ddt,  $J$  = 16.8, 10.2, 6.5 Hz, 1H), 5.08 (dq,  $J$  = 17.1, 1.6 Hz, 1H), 5.00 (dd,  $J$  = 10.2, 1.5 Hz, 1H), 3.86 (s, 3H), 3.03 – 3.00 (m, 2H), 2.51 – 2.45 (m, 2H). **<sup>13</sup>C NMR** (101 MHz,  $CDCl_3$ )  $\delta$  198.1, 163.5, 137.6, 130.4, 130.1, 115.2, 113.8, 55.5, 37.5, 28.5. **HRMS** (ESI)  $m/z$  calcd. for  $C_{12}H_{14}NaO_2$   $[M + Na^+]$  213.08860, found 213.08858.

These data are in good agreement with those reported in the literature.<sup>12</sup>



***1-(3-Fluorophenyl)pent-4-en-1-one (4i)***

Reaction performed with 2-chloro-1-(3-fluorophenyl)ethanone **1i** (193.4 mg, 1.12 mmol, 1 equiv.) and allyl alcohol (1 mL, 14.6 mmol, 15 equiv.). The residue was purified by

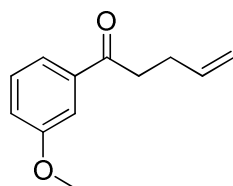
<sup>12</sup> S. Hok and N. E. Schore, *J. Org. Chem.*, 2006, **71**, 1736.

column chromatography on silica gel (eluent: cyclohexane/AcOEt = 95/5) and yielded 73 mg (37%) of the expected product **4i** as a yellow oil.

Data for **4i**:

**IR** (ATR Diamond): 3076, 2927, 2358, 1690, 1588, 1442, 1260, 1158, 996, 910, 784  $\text{cm}^{-1}$ ;  **$^1\text{H}$  NMR** (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.74 (ddd,  $J = 7.8, 1.4, 1.1$  Hz, 1H), 7.65 (ddd,  $J = 9.5, 2.5, 1.6$  Hz, 1H), 7.45 (td,  $J = 7.9, 5.5$  Hz, 1H), 7.32 – 7.22 (m, 1H), 5.90 (ddt,  $J = 16.8, 10.2, 6.5$  Hz, 1H), 5.10 (dq,  $J = 17.1, 1.6$  Hz, 1H), 5.03 (dq,  $J = 10.2, 1.3$  Hz, 1H), 3.08 – 3.05 (m, 2H), 2.54 – 2.48 (m, 2H).  **$^{13}\text{C}$  NMR** (101 MHz,  $\text{CDCl}_3$ )  $\delta$  198.2, 163.0 (d,  $J = 247.9$  Hz), 139.1 (d,  $J = 6.1$  Hz), 137.1, 130.4 (d,  $J = 7.6$  Hz), 123.9 (d,  $J = 3.0$  Hz), 120.1 (d,  $J = 21.5$  Hz), 115.6, 114.9 (d,  $J = 22.3$  Hz), 38.0, 28.1. **HRMS** (ESI)  $m/z$  calcd. for  $\text{C}_{11}\text{H}_{11}\text{FNaO}$  [ $\text{M} + \text{Na}^+$ ] 201.06861, found 201.06835.

These data are in good agreement with those reported in the literature.<sup>13</sup>



***1-(3-Methoxyphenyl)pent-4-en-1-one (4j)***

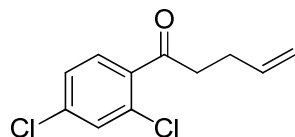
Reaction performed with 2-chloro-1-(3-methoxyphenyl)ethanone **1j** (185 mg, 1.00 mmol, 1 equiv.) and allyl alcohol (1 mL, 14.6 mmol, 15 equiv.). The residue was purified by column chromatography on silica gel (eluent: cyclohexane/AcOEt = 95/5) and yielded 70 mg (37%) of the expected product **4j** as a yellow oil.

Data for **4j**:

**IR** (ATR Diamond): 3075, 2938, 2841, 2358, 1685, 1589, 1432, 1260, 1171, 1039, 914, 874, 780  $\text{cm}^{-1}$ ;  **$^1\text{H}$  NMR** (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.56 – 7.49 (m, 2H), 7.37 (t,  $J = 7.9$  Hz, 1H), 7.11 (ddd,  $J = 8.2, 2.7, 0.9$  Hz, 1H), 5.91 (ddt,  $J = 16.8, 10.2, 6.5$  Hz, 1H), 5.09 (dq,  $J = 17.1, 1.6$  Hz, 1H), 5.02 (dq,  $J = 10.2, 1.3$  Hz, 1H), 3.86 (s, 3H), 3.08 – 3.05 (m, 2H), 2.53 – 2.47 (m, 2H).  **$^{13}\text{C}$  NMR** (101 MHz,  $\text{CDCl}_3$ )  $\delta$  199.3, 159.9, 138.4, 137.4, 129.6, 120.7, 119.5, 115.4,

112.4, 55.5, 37.9, 28.3. **HRMS** (ESI)  $m/z$  calcd. for  $C_{12}H_{14}NaO_2$   $[M + Na^+]$  213.08860, found 213.08844.

These data are in good agreement with those reported in the literature.<sup>13</sup>

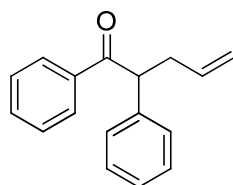


***1-(2,4-Dichlorophenyl)pent-4-en-1-one (4k)***

Reaction performed with 2-chloro-1-(2,4-dichlorophenyl)ethanone **1k** (220.8 mg, 0.99 mmol, 1 equiv.) and allyl alcohol (1 mL, 14.6 mmol, 15 equiv.). The residue was purified by column chromatography on silica gel (eluent: cyclohexane/AcOEt = 90/10) and yielded 81 mg (36%) of the expected product **4k** as a yellow oil.

Data for **4k**:

**IR** (ATR Diamond): 3079, 2923, 2358, 1696, 1582, 1372, 1272, 1200, 1104, 982, 915, 820  $cm^{-1}$ ; **<sup>1</sup>H NMR** (400 MHz,  $CDCl_3$ )  $\delta$  7.45 – 7.42 (m, 2H), 7.32 (dd,  $J$  = 8.3, 2.0 Hz, 1H), 5.86 (ddt,  $J$  = 16.8, 10.2, 6.5 Hz, 1H), 5.10 – 5.00 (m, 2H), 3.04 (t,  $J$  = 7.3 Hz, 2H), 2.50 – 2.45 (m, 2H). **<sup>13</sup>C NMR** (101 MHz,  $CDCl_3$ )  $\delta$  201.4, 137.7, 137.4, 136.7, 132.1, 130.5, 130.2, 127.4, 115.8, 42.1, 28.2. **HRMS** (ESI)  $m/z$  calcd. for  $C_{11}H_{10}Cl_2NaO$   $[M + Na^+]$  250.99991, found 251.00009.



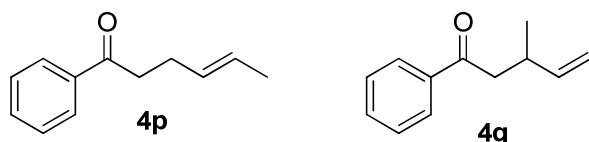
***1,2-Diphenylpent-4-en-1-one (4l)***

Reaction performed with 2-chloro-1,2-diphenylethanone **1l** (230.1 mg, 1.00 mmol, 1 equiv.) and allyl alcohol (1 mL, 14.6 mmol, 15 equiv.). The residue was purified by column chromatography on silica gel (eluent: cyclohexane/ $CH_2Cl_2$  = 20/80) and yielded 77 mg (33%) of the expected product **4l** as a yellow oil.

<sup>13</sup> L. E. Overman et A. E. Renaldo, *J. Am. Chem. Soc.*, 1990, **112**, 3945.

Data for **4l**:

**IR** (ATR Diamond): 3068, 2922, 2358, 1681, 1595, 1493, 1447, 1343, 1245, 1205, 1074, 993, 917, 753, 697  $\text{cm}^{-1}$ ;  **$^1\text{H}$  NMR** (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.99 – 7.96 (m, 2H), 7.52 – 7.47 (m, 1H), 7.43 – 7.38 (m, 2H), 7.30 – 7.32 (m, 4H), 7.24 – 7.20 (m, 1H), 5.77 (ddt,  $J$  = 17.1, 10.2, 6.9 Hz, 1H), 5.06 (dq,  $J$  = 17.1, 1.5 Hz, 1H), 4.99 (ddt,  $J$  = 10.2, 2.0, 1.1 Hz, 1H), 4.65 (t,  $J$  = 7.3 Hz, 1H), 2.97 (dddt,  $J$  = 14.5, 7.9, 6.9, 1.2 Hz, 1H), 2.59 (dt,  $J$  = 14.3, 6.9, 1.3 Hz, 1H).  **$^{13}\text{C}$  NMR** (101 MHz,  $\text{CDCl}_3$ )  $\delta$  199.3, 139.2, 136.8, 136.1, 133.0, 129.0, 128.8, 128.6, 128.3, 127.2, 116.8, 53.7, 38.3. **HRMS** (ESI)  $m/z$  calcd. for  $\text{C}_{17}\text{H}_{16}\text{NaO}$  [ $\text{M} + \text{Na}^+$ ] 259.10934, found 259.10973.

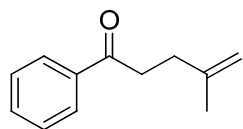


**4-Methyl-1-phenylpent-4-en-1-one (4p, 4q)**

Reaction performed with  $\alpha$ -chloroacetophenone **1a** (77.4 mg, 0.50 mmol, 1 equiv.) and, (*E*)-but-2-en-1-ol (1.3 mL, 15.2 mmol, 30 equiv.). The residue was purified by column chromatography on silica gel (eluent: pentane/ $\text{CH}_2\text{Cl}_2$  = 90/10) and yielded 44 mg (50%) of a mixture (80/20) of the linear **4p** and the branched products **4q** as a yellow oil.

Data for **4p, 4q**:

**IR** (ATR Diamond): 2924, 2856, 1733, 1687, 1594, 1448, 1364, 1264, 1205, 968  $\text{cm}^{-1}$ ;  **$^1\text{H}$  NMR** (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.98 – 7.95 (m, 2H (**4p**) + 2H (**4q**)), 7.58 – 7.54 (m, 1H (**4p**) + 1H (**4q**)), 7.49 – 7.45 (m, 2H (**4p**) + 2H (**4q**)), 5.86 (ddd,  $J$  = 17.0, 10.4, 6.4 Hz, 1H (**4q**)), 5.52–5.50 (m, 2H (**4p**)), 5.04 (dt,  $J$  = 17.3, 1.3 Hz, 1H (**4q**)), 4.99 – 4.94 (m, 1H (**4q**)), 3.06 – 3.02 (m, 2H (**4p**) + 1H (**4q**)), 2.94 – 2.88 (m, 1H (**4q**)), 2.50 (m, 1H (**4q**)), 2.46 – 2.40 (m, 2H (**4p**)), 1.64–1.66 (m, 3H (**4p**)), 1.11 (d,  $J$  = 6.4 Hz, 3H (**4q**)).  **$^{13}\text{C}$  NMR** (101 MHz,  $\text{CDCl}_3$ )  $\delta$  199.9, 196.4, 143.2, 137.1, 133.0, 133.0, 130.1, 129.9, 128.7, 128.2, 128.1, 126.0, 113.1, 45.3, 38.7, 33.7, 27.3, 19.9, 18.0. **HRMS** (ESI)  $m/z$  calcd. for  $\text{C}_{12}\text{H}_{14}\text{NaO}$  [ $\text{M} + \text{Na}^+$ ] 197.09369, found 197.09358.



***4-Methyl-1-phenylpent-4-en-1-one (4r)***

Reaction performed with  $\alpha$ -chloroacetophenone **1a** (78.1 mg, 0.50 mmol, 1 equiv.) and 2-methylprop-2-en-1-ol (1.3 mL, 15.4 mmol, 30 equiv.). The residue was purified by column chromatography on silica gel (eluent: cyclohexane/AcOEt = 95/5) and yielded 45 mg (51%) of the expected product **4r** as a yellow oil.

Data for **4r**:

**IR** (ATR Diamond): 2924, 2853, 2360, 2341, 1725, 1686, 1650, 1558, 1448, 1360, 1202, 967, 888  $\text{cm}^{-1}$ .  **$^1\text{H}$  NMR** (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.99 – 7.97 (m, 2H), 7.59 – 7.54 (m, 1H), 7.49 – 7.45 (m, 2H), 4.77 (s, 1H) 4.72 (s, 1H), 3.15 – 3.11 (m, 2H), 2.48 – 2.44 (m, 2H), 1.79 (s, 3H).  **$^{13}\text{C}$  NMR** (101 MHz,  $\text{CDCl}_3$ )  $\delta$  199.8, 144.8, 137.1, 133.1, 128.7, 128.1, 110.3, 36.9, 32.0, 22.8. **HRMS** (ESI)  $m/z$  calcd. for  $\text{C}_{12}\text{H}_{14}\text{NaO}$  [ $\text{M} + \text{Na}^+$ ] 197.09369, found 197.09363.

III. Spectra

